

THE
VOLUMETRIC
DETERMINATION OF BISMUTH
AS
MOLYBDATE
AND
ITS SEPARATION FROM COPPER

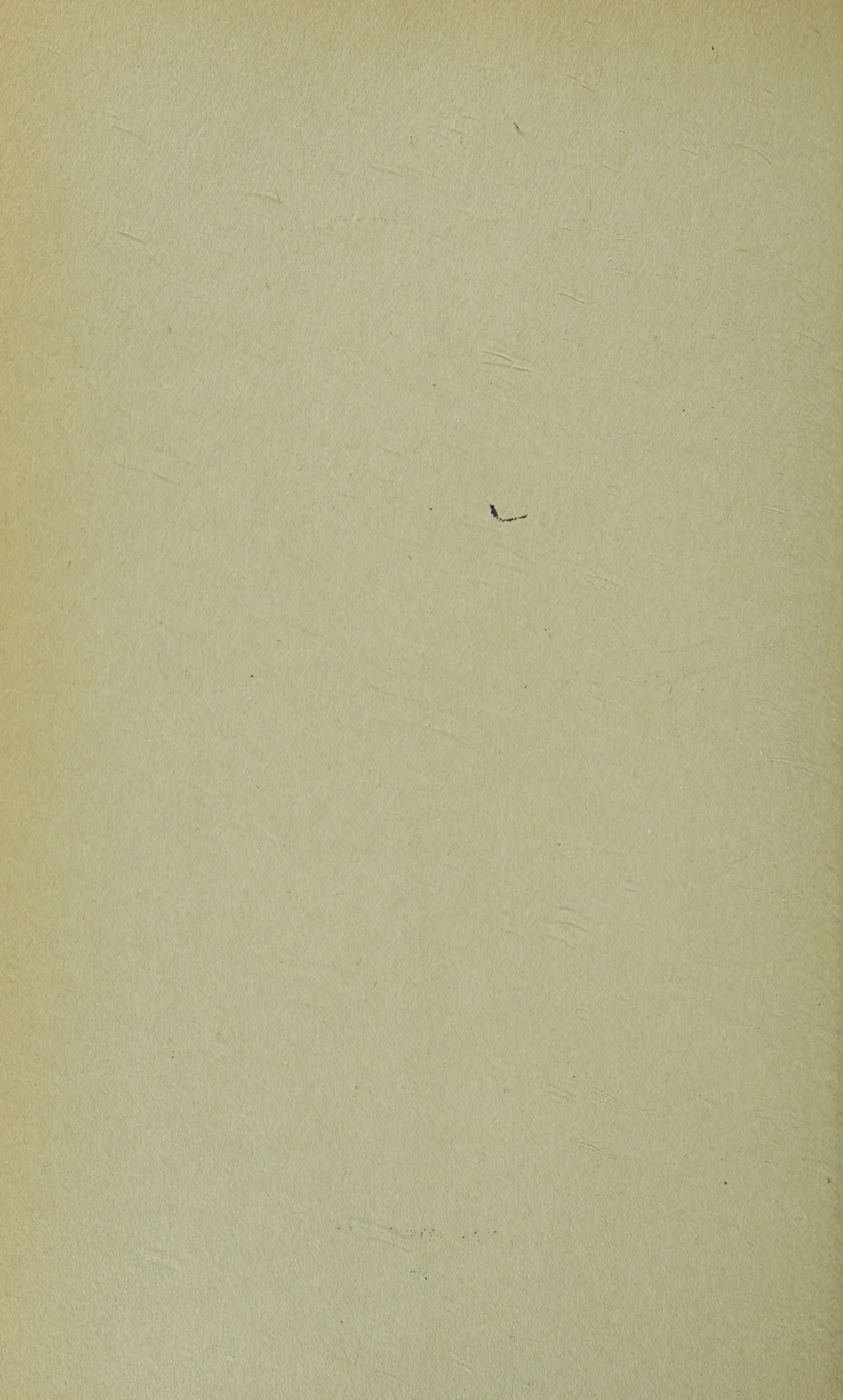
By
HERMAN S. RIEDERER, B.S., A.M.

DISSERTATION

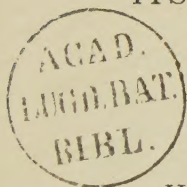
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY UNDER THE FACULTY OF PURE SCIENCE OF
COLUMBIA UNIVERSITY

NEW YORK CITY

1902



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INTRODUCTION.

At the present time the quantitative determination of bismuth is conducted in the great majority of cases by precipitation as bismuth basic carbonate by ammonium carbonate, in spite of the fact that many different schemes have been published for its separation from other metals and for determination, using other reagents. These may all be classed under one of the following sub-divisions, gravimetric, volumetric and electrolytic.

It was with the intention of finding a reliable method equal in accuracy to the carbonate, and volumetric if possible that this work was undertaken.

As the work progressed and the molybdate method was to be applied to ores, to show its practical value, it developed that a shorter and simpler separation of bismuth from copper especially, would make the method complete from the ore, and it was then that the precipitation of bismuth from a solution containing tartaric acid and alkaline with caustic potash and potassium cyanide by using hydrogen sulphide was worked out and found satisfactory.

ACKNOWLEDGEMENT.

This work was carried out under the direction of Professor Edmund H. Miller.

It is with great pleasure that I take this opportunity for thanking him for his ready counsel and kind encouragement which he extended to me throughout this research.

H. S. R.

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November 1, 1902.

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BISMUTH.

History and Occurrence.

Bismuth has been known for a very long time as Marcasite, although at times it was confused with other shining metals. The first scientific note about bismuth was made by Basilius Valentinus in the 15th century, who described it as a metallic body. Later Paracelus described it as Wisemuth and Agricola in 1530 as Bisemutum. As late as 1675 Lemery confused it with zinc. Then its properties were investigated by Stahl, Cronsted and Kirwan, Potts in 1730 and Geoffroy in 1753. The reactions of bismuth were made known by Bergmann in 1784 as those of a peculiar metal and the knowledge of the metal and its compounds was greatly enlarged by the work of Berzelius.

Bismuth occurs as the native metal, as the sulphides Bismuthinite and Aikinite, the telluride Tetradyomite, the oxide Bismite and the carbonate Bismutite. It is usually found associated with other minerals chiefly those of copper, lead and iron, also tin and cobalt.

THE QUANTITATIVE DETERMINATION OF BISMUTH.

I. HISTORICAL.

Precipitation of the Sulphide.

It was long known that hydrogen sulphide will precipitate all the bismuth from a weakly acid solution as the trisulphide Bi_2S_3 and this was used as the quickest way. Naturally this was exceedingly incorrect due to the contamination by free sulphur, and so treatments with sodium sulphite or carbon disulphide were used, and the residual sulphide was weighed. Even here great uncertainty exists as to the complete removal of free sulphur and also as the bismuth sulphide will oxidize even at 100°C .

Precipitation of the Basic Carbonate.

When a solution of bismuth is made alkaline with ammonia the oxyhydrate is precipitated, which is readily changed to the basic carbonate by adding ammonium carbonate and boiling. This precipitate is easily filtered and washed and for determination is usually ignited in a porcelain crucible to the trioxide. This is the method which is now used as it is a simple means of separating bismuth from copper. In the presence of much copper, two, three or even four precipitations may be necessary to get the bismuth free from all copper.

Precipitation of Bismuth Chromate.

This method, proposed by J. Löwe,¹ consists in precipitating bismuth from a nearly neutral nitrate solution with potassium dichromate in slight excess, heating, and then boiling the precipitate with successive portions of water and decanting through

¹ Jour. f. pract. Chem. vol. 67, p. 464.

a weighed filter. The precipitate is dried at 120°C . Its composition is $(\text{BiO})_2\text{Cr}_2\text{O}_7$.

Precipitation of Bismuth Oxychloride.

This is another old method consisting of precipitating bismuth from a chloride solution by great dilution when the amount of free acid is not enough to hold it in solution. When nitrate solution is used ammonium chloride must be added. The method is claimed to be exact although no satisfactory results could be obtained. The method is inconvenient owing to the great bulk of liquid which must be filtered for each determination.

Salkowski,¹ precipitated bismuth as arsenate which was dried and weighed.

Besides these gravimetric methods of determination, numerous reactions have been used for separations of bismuth from other metals or groups. Some of these follow:

Jannasch with others used peroxide of hydrogen to separate bismuth from the following metals: Silver, mercury, copper, cadmium, cobalt, nickel and zinc.²

The volatility of bismuth bromide and chloride was utilized for separations by the following:

1874. Vogel, bismuth from lead as chloride.³

1891. Remmler, same.⁴

1891. Jannasch, from cadmium as bromide.⁵

1892. Jannasch, from lead and cadmium as bromide.⁶

1895. Jannasch, from cobalt, nickel, zinc and copper, with bromine and carbon dioxide.⁷

1896. Jannasch, from the copper and iron groups with hydrochloric acid.⁸

¹ Z. analyt. Chem. vol. 8, p. 205, 1869.

² Berichte vols. 26, 27 and 28, 1893, 1894 and 1895; and Z. anorg. Chem. vol. 8, p. 302, 1895.

³ Z. analyt. Chem. vol. 13, p. 60.

⁴ Berichte, vol. 24, p. 3554.

⁵ Berichte vol. 24, p. 3746.

⁶ Berichte, vol. 25, pp. 124 and 736.

⁷ Berichte, vol. 28, p. 792.

⁸ Berichte, vol. 29, p. 698.

1896. Moyer, from lead, copper, cadmium, zinc, silver, nickel and cobalt with hydrochloric acid.¹

The reduction of bismuth in solution to the metal has been tried by several, by the use of various reagents as follows:

1866. Patera, lead strips.²

1896. Muthmann and Mawraw, hypophosphorus acid.³

1898. Vanino and Treubert, formaldehyde.⁴

1898. Jannasch and Devin, hydroxylamine.⁵

1899. Clark, steel turnings.⁶

Classen in his latest book,⁷ does not think it worth the time and space to mention more about volumetric and electrolytic methods for bismuth, than a note saying that none of the methods of either type are satisfactory. Treadwell⁸ makes a similar statement. A few will be noted here as reference will be made to them later on in the work.

In 1877 Pattison Muir published a method⁹ by which bismuth is precipitated as oxalate, changed by boiling to the basic oxalate, $\text{Bi}_2\text{O}(\text{C}_2\text{O}_4)_2$ which after solution in acid is titrated with potassium permanganate.

In 1882 Muir¹⁰ changed the foregoing method by precipitating a double potassium and bismuth oxalate and titrating the excess with potassium permanganate.

For electrolytic determination, a variety of solutions and conditions have been proposed, as the use of glycerine and a rotating anode, Wimmenauer,¹¹ deposition of amalgam, Vortmann,¹² also sulphate, nitrate, phosphate, tartrate, citrate and

¹ J. Am. Chem. Soc. vol. 18, pp. 1029-44.

² Berggeist, 1866, No. 28, abst. Z. analyt. Chem. vol. 5, p. 226.

³ Berichte, vol. 29, p. 1162.

⁴ Berichte, vol. 31, p. 1303.

⁵ Berichte, vol. 31, p. 2377.

⁶ J. Soc. Chem. Ind. vol. 19, p. 26.

⁷ Ausgewählte Methoden d. Analyt. Chem., 1901.

⁸ Analytische Chemie, vol. 2, 1902.

⁹ J. Chem. Soc. London, vol. 33, p. 70, 1878.

¹⁰ J. Chem. Soc. London, vol. 41, p. 1.

¹¹ Z. anorg. Chem. vol. 27, p. 1, 1901.

¹² Berichte, vol. 24, p. 2759, 1891.

oxalate solutions. The latest work has just been completed by Kammerer at the University of Pennsylvania.¹

II. EXPERIMENTAL.

About six liters of a bismuth nitrate solution containing approximately 1% metal were prepared. This solution was standardized as accurately as possible, and was used in all further work, except where otherwise noted.

a. Direct Evaporation and Ignition.

The bismuth nitrate solution was first evaporated to dryness on the water bath, then heated in an air bath to 120°-130°C. to facilitate the ignition which followed. Both porcellain and platinum vessels were used as indicated.

Results :

taken Bi(NO ₃) ₃	Character of vessel.	Bi ₂ O ₃	found =	Bi
5 c.c.	porcellain.	0.0643 gm.		0.05765 gm.
5 c.c.	"	0.0643 gm.		0.05765 gm.
6 c.c.	"	0.0773 gm.		0.06931 gm.
20 c.c.	platinum.	0.2578 gm.		0.23084 gm.
30 c.c.	"	0.3663 gm.		0.34636 gm.

b. Precipitation as Basic Carbonate.

Portions of the bismuth nitrate solution were diluted to about 400 c.c., ammonia was added to alkaline reaction, and then ammonium carbonate. The whole was then heated to near boiling. The basic carbonate was filtered, washed and dried. The paper was burnt separate from the precipitate in a porcellain crucible, with addition of a few drops of nitric acid. The residue with the precipitate added was then ignited to the trioxide Bi₂O₃. Large amounts of bismuth require heating for some time to insure complete conversion to the trioxide.

¹ Thesis, 1902.

Results:

taken $\text{Bi}(\text{NO}_3)_3$	Bi_2O_3	found =	Bi
20 c.c.	0.2581 gm.		0.23140 gm.
20 c.c.	0.2577 gm.		0.23106 gm.
20 c.c.	0.2570 gm.		0.23042 gm.
25 c.c.	0.3222 gm.		0.28888 gm.
30 c.c.	0.3869 gm.		0.34689 gm.
10 c.c.	0.1288 gm.		0.11548 gm.
11 c.c.	0.1415 gm.		0.12687 gm.
12 c.c.	0.1542 gm.		0.13826 gm.

From these results and those obtained by method (a) the strength of the bismuth nitrate solution was taken to be: 1 c.c. = 0.01155gm. Bi. This result was further confirmed by the ignition of precipitated bismuth sulphide (see below), and also indirectly by the molybdate titration method.

c. Precipitation of Bismuth Sulphide.

Known volumes of the standard solution were diluted to about 500 c.c. and were saturated with hydrogen sulphide gas. The precipitated bismuth sulphide was filtered and washed, and then treated with carbon disulphide, to extract sulphur. The residue was weighed after careful drying at 100°C.

Results:

taken $\text{Bi}(\text{NO}_3)_3$	=	Bi	Bi_2S_3	found =	Bi
20 c.c.		0.2310 gm.	0.2949 gm.		0.2395 gm.
20 c.c.		0.2310 gm.	0.2963 gm.		0.2407 gm.

These precipitates had been filtered on Gooch crucibles and after weighing, they were ignited to bismuth trioxide.

Results:

taken $\text{Bi}(\text{NO}_3)_3$	=	Bi	Bi_2O_3	found =	Bi
20 c.c.		0.2310 gm.	0.2575 gm.		0.23086 gm.
20 c.c.		0.2310 gm.	0.2578 gm.		0.23114 gm.

From these results it is evident that all the bismuth can be precipitated from a weakly acid solution, by saturating with hydrogen sulphide gas. The precipitate contains a large amount of free sulphur, but is easily converted to bismuth trioxide by ignition.

d. Electrolytic Deposition.

It was deemed advisable to try some of the proposed methods and that of Wimmenauer¹ looked promising. No satisfactory results could be obtained.

Before this work was completed, Kammerer's conditions were published,² and they also were tried. The conditions are as follows: Bi. 0.10-0.15 gm.; HNO_3 1 c.c. sp. gr. 1.42; H_2SO_4 2 c.c. sp.gr. 1.84; K_2SO_4 1 gm.; dilution 150 c.c.; temperature 45° - 50°C .; N.D.₁₀₀ 0.02 ampères; 2 volts. The deposition should be completed in about 8 hours. It can also be run at the above temperature for 2-3 hours and then over night. Under the given conditions, this latter scheme was more convenient. The deposit is washed with warm water by siphoning, then alcohol-ether 1:2, and lastly ether.

The directions were followed as closely as possible but the results were unsatisfactory except in a single analysis. Platinum gauze electrodes were used with no better success.

The practical value of the method is doubtful as much time is necessary to get the solution into the right conditions. When .10-.15 gm. of bismuth are present in an analysis as any precipitate, more than 1 c.c. nitric acid will be used to dissolve it, and therefore the solution will have to be evaporated to remove the excess of nitric acid. As the voltage and ampèrage must be closely regulated, too much adjustment is necessary for practical work, although good results are sometimes obtained with it.

¹ Z. anorg. Chem. vol. 27, p. 1, 1901.

² Electrochemical Analysis, Smith 3rd Ed., 1902, p. 67.

Warwick and Kyle¹ proposed apparently as a new method to precipitate bismuth as oxalate either with ammonium oxalate or oxalic acid, and heating to facilitate the reaction. The clear solution is then decanted, and the precipitate is boiled with successive portions of water to convert the precipitate to the basic oxalate. This is then dissolved in acid and the oxalic acid is titrated with standard potassium permanganate solution. Both ammonium oxalate and oxalic acid precipitate bismuth as oxalate, which however is easily soluble in excess of ammonium oxalate whether hot or cold. Owing to this fact, ammonium oxalate was not further tried in determining the value of the proposed method. Oxalic acid was then tried as described by Warwick and Kyle.

It was noted that this is nearly an exact copy of Muir's method.² The only great difference between them is that in Muir's method the precipitation is done in the cold, while Warwick and Kyle make their precipitation by heating, and also claim that two boilings with 50 c.c. water suffice to convert all the precipitate to the basic salt, while Muir says to boil with successive portions of water till the filtrates are free from acid. In the following experiments it was found that only very small amounts of oxalate could be converted by two boilings, while even 0.0924 gm. bismuth and over required three and four boilings with 80-100 c.c. water to remove all free acid. The results in the following table were obtained by the factor calculated as given in the method by Warwick and Kyle.

If 1 c.c. $\text{KMnO}_4 = 0.010$ gm. Fe it is equivalent to 0.0186 gm. Bi. The KMnO_4 used was 1 c.c. = 0.005612 gm. Fe and hence equivalent to 0.01048 gm. Bi. This was the factor used. To show the irregularity of the results, the last column in the table shows what the factor for KMnO_4 to Bi should be in each case according to the results obtained.

¹ E. and M. J., Apr. 1901.

² J. Chem. Soc. London, vol. 33, p. 70, 1878.

Results :

$\text{Bi}(\text{NO}_3)_3$	taken =	Bi	used KMnO_4	found Bi	calculated factors.
4 c.c.		0.0451 gm.	3.8 c.c.	0.0398 gm.	0.01186
6 c.c.		0.0693 gm.	5.6 c.c.	0.0587 gm.	0.01237
8 c.c.		0.0924 gm.	8.4 c.c.	0.0878 gm.	0.01100
10 c.c.		0.1155 gm.	9.6 c.c.	0.1006 gm.	0.01203
12 c.c.		0.1386 gm.	12.4 c.c.	0.1300 gm.	0.01117

These results being irregularly low the cause was sought in the solubility of the oxalate. It was then found that the bismuth oxalate is slightly soluble in a hot solution acid with oxalic acid. Apparently this fact was known to Muir, as in his method the bismuth is precipitated in the cold and the supernatant liquid is decanted. Then the precipitate free from oxalic acid solution is converted to the basic oxalate by boiling with water. The method was tried to ascertain its exactness so that it might be used for further standardization if necessary. The results however were irregularly high due to the difficulty experienced in converting to the basic salt. The precipitate is very fine and heavy and caused violent bumping. Four or more boilings were always necessary to free the washings of oxalic acid, so that no test was obtained. The conversion had however not been completed.

Results :

$\text{Bi}(\text{NO}_3)_3$	taken =	Bi	used KMnO_4	found Bi
4 c.c.		0.0451 gm.	4.6 c.c.	0.0482 gm.
6 c.c.		0.0693 gm.	7.25 c.c.	0.0775 gm.
8 c.c.		0.0924 gm.	10.3 c.c.	0.1079 gm.
10 c.c.		0.1155 gm.	11.7 c.c.	0.1226 gm.
12 c.c.		0.1386 gm.	14.8 c.c.	0.1551 gm.
14 c.c.		0.1619 gm.	16.7 c.c.	0.1750 gm.
8.1 c.c.		0.0936 gm.	9.7 c.c.	0.1016 gm.
9.9 c.c.		0.1080 gm.	11.95 c.c.	0.1252 gm.
4 c.c.		0.0451 gm.	4.35 c.c.	0.0456 gm.
6 c.c.		0.0693 gm.	7.3 c.c.	0.0765 gm.
14 c.c.		0.1619 gm.	16.75 c.c.	0.1755 gm.

In the last three determinations the precipitates were boiled several times after the conversion seemed to be complete. These show an approximation to the theoretical figures, but the method did not seem practical for further work, as three other determinations started with these last three, were lost by the violent bumping already mentioned.

Warwick and Kyle also claim that this method is a separation of bismuth from copper, arsenic, antimony and several other metals. Copper being the most important, its behavior with ammonium oxalate and also oxalic acid was tried and it was found to act like bismuth in both cases, namely, soluble in excess of ammonium oxalate and insoluble in oxalic acid. After obtaining these results, it was not thought necessary to test the method of Warwick and Kyle any further

1° as the principle of the method is old,

2° as the proposed changes make the method altogether wrong, and

3° as the separations claimed are impossible owing to the reactions of the elements with the reagents employed.

These conclusions are further confirmed by Grabill,¹ who made a study of the reaction of bismuth with ammonium oxalate. He contradicts Warwick and Kyle, and also states that copper oxalate is insoluble.

Another proof that the separation of bismuth and copper is impossible by oxalic acid is given by the fact that Peters² precipitates copper quantitatively with this reagent and determines copper in this way.

¹ E. and M. J., vol. 72, p. 354, 1901.

² Z. anorg. Chem. vol. 26, p. 111, 1901.

When a solution of ammonium molybdate in nitric acid is added to bismuth nitrate and the whole is then neutralized with ammonia but not made alkaline, all the bismuth is precipitated as a molybdate in a fine flocculent form. If this is then warmed without boiling, the whole precipitate will collect into large heavy flocks which settle very rapidly. This precipitate is easily washed by decantation and filters very readily. By the following work it was found that the molybdenum ratio to that of bismuth remained constant.

The limits for the precipitation are very narrow. The ammonium molybdate must be in large excess, three to four times the theoretical amount necessary for combining with all the bismuth. The solution must be just acid with nitric acid. To obtain this point methyl orange was found very satisfactory as an indicator to get the solution neutral, and it was then acidified with one or two drops of 30% nitric acid. The whole is then heated on a thick asbestos pad over a small flame until the fine flocks have collected; generally the whole precipitate will rise from the bottom in large masses by the action of the hot circulating solution. The precipitate was then stirred to break it up, after which it was allowed to stand to let it settle. The precipitate is exceedingly heavy and settled in a few seconds, forming a compact mass. The supernatant liquid which must be perfectly clear is decanted through a plain filter paper. Then the precipitate is washed twice by decantation with a 3% solution of ammonium sulphate, after which it is washed onto the filter with the ammonium sulphate solution. It is then dissolved in dilute sulphuric acid and run through a Jones' reductor with suction; after this it is strongly acidified with sulphuric acid and is immediately titrated with standard KMnO_4 solution.

The precipitation and washing, was done in a small beaker and the bulk was about 200 c.c. It was found best to heat slowly, as with fast heating the solution was liable to come to a boil, which makes the determination unreliable. A 3% solution of ammonium sulphate was found satisfactory for washing and was preferred to any other salt as it only has constituents

of the solution which is run through the reductor and as ammonium sulphate is inactive to zinc in acid solution and also to KMnO_4 . A reductor with a column of zinc 40-45 cm. in length in a tube 1.25 cm. in diameter was used to avoid the necessity of more than one passage through the zinc, and the suction flask was so large that the titration was also made in it directly. Thus air had the least chance of reoxidizing the molybdous oxide Mo_2O_3 which was to be determined by KMnO_4 .

The color of the molybdate precipitate is pure white. Sometimes when the conditions were not followed exactly, a slightly yellowish to canary yellow compound resulted which gave varying results, but always lower than the white compound. This yellow molybdate when formed could however easily be changed to the white, by first making the solution alkaline with ammonia to throw out bismuth oxyhydrate and then dissolving this in nitric acid, all this being done in the whole mixture of precipitate and solution. The clear solution is now retreated as a new solution except that it is not always necessary to add more ammonium molybdate.

The results given in the following tables are calculated for the factor, the equivalent in bismuth of 1 c.c. of the KMnO_4 solution. To compare the results obtained in this way with an absolute standard, several samples of the purest obtainable bismuth were weighed out and treated like the standard $\text{Bi}(\text{NO}_3)_3$ solution with very satisfactory results.

Results :

Bi(NO ₃) ₃		taken	Bi.	used	Equivalent amount
		=		KMnO ₄	of bismuth of 1 c.c. KMnO ₄
9	c.c.		0.10395 gm.	28.5 c.c.	0.003647
9	c.c.		0.10395 gm.	28.7 c.c.	0.003621
15	c.c.		0.17325 gm.	47.75 c.c.	0.003628
16	c.c.		0.18480 gm.	50.9 c.c.	0.003630
8.5	c.c.		0.09818 gm.	27. c.c.	0.003636
12.3	c.c.		0.14207 gm.	30.8 c.c.	0.004610*
7.8	c.c.		0.09009 gm.	24.8 c.c.	0.003632
9.8	c.c.		0.11319 gm.	31.15 c.c.	0.003633
11.6	c.c.		0.13398 gm.	30. c.c.	0.004466*

* These two precipitates were yellow, but they were titrated like the others to see what their character is. The results indicate a more basic compound than the white precipitate.

The following results were obtained on samples of metallic bismuth :

Results :

taken Bi	used KMnO ₄	factor (as above)
0.1100 gm.	30.1 c.c.	0.003654
0.1398 gm.	38.3 c.c.	0.003626
0.1084 gm.	29.8 c.c.	0.003637
0.1434 gm.	39.5 c.c.	0.003630
0.1815 gm.	50.0 c.c.	0.003630

From these results the factor for the KMnO₄ on hand was taken to be: 1 c.c. = 0.003630 gm. Bi. This made the ratio of Bi : Mo in the compound 1 : 1.92

Method of Calculation

Fe standard : Mo standard :: 3 Fe : 1 Mo.

0.005612 : x :: 3 x 55.9 : 96

x = 0.0032126

hence 0.0032126 gm. Mo = 0.003630 gm. Bi

or 1 Bi : 1.92 Mo.

This ratio being exceedingly complex, it was determined gravimetrically as follows: 10 c.c. Bi(NO₃)₃ solution was measured out and precipitated as molybdate, as usual. This was decomposed with ammonium sulphide, which precipitated bismuth sulphide and held the molybdenum sulphide in solution. The bismuth sulphide was dissolved with hot dilute nitric acid into a weighed platinum dish, in which the bismuth was determined as by the evaporation method (a) (p. 5) as a check on the completeness of precipitation by ammonium molybdate. The molybdenum solution was acidified, saturated with hydrogen sulphide and heated in boiling water, in a tightly stoppered bottle. The precipitated molybdenum sulphide was filtered in a weighed platinum Gooch crucible, washed with sulphuric acid water and then alcohol. The sulphide was then carefully ignited to the oxide MoO₃ and weighed.

Results:

	A	B	C	D
Bi ₂ O ₃ found	0.1289 gm.	0.1285 gm.	0.1290 gm.	0.1292 gm.
= Bi	0.11557gm.	0.11521gm.	0.11568gm.	0.11584gm.
MoO ₃ found	0.1589 gm.	0.1587 gm.	0.1586 gm.	0.1373 gm.
= Mo	0.10583gm.	0.10579gm.	0.10572gm.	0.09152gm.
Molecular ratio Bi ¹	.000555	.0005536	.0005558	.0005565
Molecular ratio Mo ¹	.001102	.001102	.001101	.0009512
Ratio Bi : Mo	1 : 1.985	1 : 1.990	1 : 1.982	1 : 1.71

Ratios A, B and C are practically equal to 1 : 2, Precipitates A, B and C were white, D was yellow, D was analysed to further prove the more basic character of the yellow compound, as already mentioned in the volumetric work.

The ratio of bismuth and molybdenum in the compound having been found to be 1 : 2 it was evident that some other element or compound entered into the composition of the precipitate. It also showed that this molybdate was unknown in literature, as the only molybdate of bismuth that could be found was the normal molybdate, ratio 2 : 3, a yellow compound soluble in 500 parts of water.² It was naturally supposed that ammonium was the missing factor in the compound, as no other base was employed. Attempts were made to obtain the molybdate pure and free from ammonium sulphate, so that the ammonia in combination could be determined. This was not found possible as both water and 50% alcohol decomposed the compound and no other available liquid could be found with which the ammonium sulphate could be washed out leaving the pure molybdate behind. This peculiarity of the compound made it necessary to make an indirect determination for ammonia, by finding the total in the compound and combined as sulphate; then determining the sulphuric acid present and calculating its equivalent of ammonia; this subtracted from the total ammonia would give the ammonia in combination. A definite amount of bismuth was employed every time to avoid

¹ Value obtained by dividing the weight of metal by its atomic weight.

² Storer's Dict. of Solubilities.

the necessity of determining this and molybdenum in each portion. The procedure of the analysis was as follows: Certain volumes of standard $\text{Bi}(\text{NO}_3)_3$ solution were measured out and precipitated as usual and washed thoroughly with ammonium sulphate solution 3%; after allowing to drain for a few minutes, the precipitate was dissolved through the paper, with dilute hydrochloric acid, into a 500 c.c. Kjeldhal flask, from which the total ammonia was distilled into standard sulphuric acid after the contents of the flask had been made alkaline with caustic soda. The excess of standard acid was titrated with standard alkali, and from this the total ammonia was calculated. The residue in the flask was acidified with hydrochloric acid and the sulphuric acid was precipitated hot with barium chloride. The barium sulphate was washed, ignited and weighed as usual. From this the SO_3 as ammonium sulphate was calculated, and also the equivalent amount of ammonia. This subtracted from the total ammonia, found by distillation, gave the amount of ammonia in combination.

The results did not check as closely as might be desired, but they indicated a common point. The error is accounted for by the great excess of ammonia in the total due to ammonium sulphate, and also, as only about 3% of the compound is ammonia if its composition is $\text{BiNH}_4(\text{MoO}_4)_2$.

Results :

A. 12 c.c. $\text{Bi}(\text{NO}_3)_3$ used = 0.1386 gm. Bi.

Titration used 45 c.c. acid = 0.09110 gm. total NH_3 .

$$\begin{array}{rcl} \text{BaSO}_4 = 0.5216 \text{ gm.} & = & 0.07616 \text{ gm. NH}_3 \text{ as } (\text{NH}_4)_2\text{SO}_4. \\ \text{difference} & & 0.01494 \text{ gm. NH}_3 \text{ in compound.} \end{array}$$

Theory for $\text{BiNH}_4(\text{MoO}_4)_2$	0.01133 gm. NH_3 .
error	+ 0.00361 gm. NH_3 .

B. 10 c.c. $\text{Bi}(\text{NO}_3)_3$ used = 0.1155 gm. Bi.

Titration used 41.7 c.c. acid = 0.070482 gm. total NH_3 .

$$\begin{array}{rcl} \text{BaSO}_4 = 0.4213 \text{ gm.} & & = 0.061399 \text{ gm. NH}_3 \text{ as } (\text{NH}_4)_2\text{SO}_4. \\ \text{difference} & & \underline{0.009083 \text{ gm. NH}_3 \text{ in compound.}} \end{array}$$

Theory for $\text{BiNH}_4(\text{MoO}_4)_2$	0.009446 gm. NH_3 .
error	— 0.000363 gm. NH_3 .

C.	30 c.c. $\text{Bi}(\text{NO}_3)_3$ used	= 0.3465 gm. Bi.
	Titration	= 0.176555 gm. total NH_3 .
	BaSO_4	= 0.141016 gm. NH_3 as $(\text{NH}_4)_2\text{SO}_4$.
	difference	0.035439 gm. NH_3 in compound.
	Theory for $\text{BiNH}_4(\text{MoO}_4)_2$	0.02834 gms. NH_3 .
	error	+ 0.007099 gms. NH_3 .

As the compound could not be obtained pure, the theoretical weight corresponding to 10 c.c. $\text{Bi}(\text{NO}_3)_3$ solution was calculated and from this the percentages of the different radicals Bi_2O_3 , MoO_3 and $(\text{NH}_4)_2\text{O}$. The last varies considerably but as the amount of ammonia in the samples used for analysis was only one-sixth to one-eighth of the total, and that had to be determined indirectly, the difficulty of getting very close results is apparent.

Results:

	Theory	A	B	C	average
Bi_2O_3	42.50 %.	42.53 %.	42.39 %.	42.56 %.	42.49 %.
MoO_3	52.74 %.	52.42 %.	52.36 %.	52.33 %.	52.37 %.
$(\text{NH}_4)_2\text{O}$	4.76 %.	6.313 %.	4.607 %.	5.987 %.	5.635 %.
	100.00 %.				100.05 %.

These results were taken to be close enough to show that the composition of the precipitate could only be $\text{BiNH}_4(\text{MoO}_4)_2$.

In what goes before this no explanation was offered for the discrepancy of the two ratios 1 : 1.92 and 1 : 1.985 for ~~iron~~ molybdenum as found by the volumetric and gravimetric methods respectively.

Looking through the recent literature on the volumetric method for phosphorus by titrating the yellow precipitate with potassium permanganate we find a difference of opinion as to the iron molybdenum factor. Babbit¹ believed the reduction to proceed to a point between Mo_2O_3 and $\text{Mo}_{12}\text{O}_{19}$ and this theory is further confirmed by Doolittle and Eavenson.² Blair and Whitfield³ then made an exhaustive investigation, not only ob-

¹ J. Analyt. Chem. vol. 7, p. 167, 1893.

² J. Am. Chem. Soc. vol. 16, p. 242, 1894.

³ J. Am. Chem. Soc. vol. 17, p. 759, 1895.

taining results themselves, but also obtaining results on the same sample of yellow precipitate from six eminent chemists. After averaging these results which agreed very well among themselves their calculations lead them to believe that in a Jones' reductor the oxide of molybdenum is $\text{Mo}_{24}\text{O}_{37}$. Possibly Mo_2O_3 is obtained as a final substance, but it is not unlikely that this would immediately reoxidize, with slight contact with air, to an extent equivalent to $\text{Mo}_{24}\text{O}_{37}$.

To see whether this would explain the difference found, the following calculation was made :

$$\begin{aligned}
 &5 \text{ Fe} = 1 \text{ KMnO}_4 \text{ in acid titration} \\
 &\text{Mo}_{24}\text{O}_{37} \text{ to } \text{MoO}_3 = 35 \text{ O} = 14 \text{ KMnO}_4 \\
 &\text{hence } 7 \text{ KMnO}_4 = 12 \text{ MoO}_3 = 35 \text{ Fe} \\
 &\text{or Fe standard : Mo standard : : } 35 \text{ Fe : } 12 \text{ Mo} \\
 &0.005612 : x : : 35 \times 55.9 : 12 \times 96. \\
 &x = 0.0033043 = \text{Mo standard.}
 \end{aligned}$$

As the ratio of bismuth to molybdenum in the compound is 1 : 2 then

$$\begin{aligned}
 &\frac{\text{Mo standard}}{2 \times \text{at. wt. Mo}} \times \text{at. wt. Bi} = \text{Bi standard for KMnO}_4 \\
 &\frac{.0033043}{192} \times 208.11 = .003582
 \end{aligned}$$

The standard found by experiment was .003630, making a difference in factors = .000048.

From this it was taken that the solution which was titrated was $\text{Mo}_{24}\text{O}_{37}$ and not Mo_2O_3 as mentioned previously. As the theoretical and experimental factors for Bi and KMnO_4 do not correspond exactly, it is advisable always to obtain the factor directly from metallic bismuth or a standard bismuth solution.

Under the conditions for the precipitation of bismuth molybdate, copper will give no apparent reaction. Attempts were made to use this for a separation of bismuth from copper. Various proportions were used of copper to bismuth, 1 : 4 to 1 : 14. In all cases the results were high, tending to show that copper does form a molybdate, which is, however soluble in the precipitant; and as the bismuth molybdate is so very bulky, the cop-

per compound cannot be wholly removed by washing whereby the result will give all the bismuth and an indefinite amount of copper.

The exactness of the molybdate method for bismuth having been proven, it was thought advisable to find a shorter separation from copper, so as to make the method of practical value if possible. The ammonium carbonate method is a perfect separation if it is repeated several times, in presence of large amounts of copper. Naturally this method is slow.

Pretzfeld,¹ in his new separation of mercury from copper, arsenic and antimony by hydrogen sulphide in a potassium cyanide solution containing tartaric acid found that among a few other metals, bismuth also interferes; he did not however determine whether it was completely precipitated. A few experiments showed that all the bismuth was thrown out of solution by Pretzfeld's conditions, namely: The acid solution is neutralized with potassium cyanide after about 30 c.c. of a saturated tartaric acid solution have been added; enough potassium cyanide must be added to dissolve any precipitate which may form except bismuth sulphide, thrown out by the sulphur in the cyanide. This alkaline solution is now saturated with hydrogen sulphide gas, and the bismuth sulphide is filtered out. The filtrate is colorless to light lemon yellow. When copper was added to the bismuth solution and the above conditions were applied, the deep red color mentioned by Pretzfeld was present every time in spite of the presence of tartaric acid. The color would not have been a serious setback for the method, had it not been due to copper; besides it was impossible to wash this copper out of the filter paper.

When the bismuth copper mixture was first made alkaline with caustic potash after adding tartaric acid, and potassium cyanide was added till the solution was clear, neither a red color appeared, nor was it necessary to use but a small amount of potassium cyanide. The solution even after saturation with hydrogen sulphide was never darker than a light lemon yellow.

¹ Dissertation. The Determination and Separation of Mercury, Columbia University, 1902.

The most important part was however that all the bismuth was precipitated as sulphide in small bulk, all copper remained in solution and the filter paper could be washed free from all copper by potassium cyanide or pure water, and pure bismuth sulphide remained.

Results :

Bi(NO ₃) ₃	taken	Cu.	Bi ₂ O ₃	found
	Bi.			Bi
10 c.c.	0.1155 gm.	0.5 gm.	0.1285 gm.	0.11521 gm.
10 c.c.	0.1155 gm.	0.5 gm.	0.1287 gm.	0.11539 gm.
10 c.c.	0.1155 gm.	1.0 gm.	0.1284 gm.	0.11512 gm.

The bismuth sulphide was dissolved in nitric acid, and then the bismuth was reprecipitated as basic carbonate which was ignited to oxide and weighed.

ANALYSIS OF BISMUTH ORES.

Two samples of bismuth ores containing iron but free from copper were obtained and these were used to show the exactness of the new method, as compared to the basic carbonate method.

From 0.3 gm. to 0.5 gm. of the richer ore were used for analysis and treated as follows: The ore was decomposed with nitric acid and was evaporated with sulphuric acid to fumes; after dilution the residue was filtered off and retreated with nitric and sulphuric acids as before. The filtrates were combined and diluted to about 750 c.c. Then bismuth sulphide was precipitated with hydrogen sulphide and filtered out. For the carbonate method this sulphide was dissolved in hot dilute nitric acid and precipitated by adding ammonia and ammonium carbonate and heating. The precipitated basic carbonate was filtered, washed and ignited in a weighed porcellain crucible. To insure against any reduction of metal by the burning of the paper, the carbonate was dissolved through the paper, into the crucible, with hot dilute nitric acid.

For the molybdate method the bismuth sulphide was also dissolved in nitric acid and this solution was treated as directed on p. 11, to free the bismuth of impurities which would interfere in the molybdate method. The pure bismuth sulphide was again dissolved in nitric acid, precipitated as molybdate, dissolved, reduced and titrated. The following results show the comparative accuracy of the two methods.

Results:

taken Ore	Bi_2O_3	=	found Bi	per cent.
0.5001 gm.	0.1096 gm.		0.0983 gm.	19.65 %.
0.5004 gm.	0.1098 gm.		0.0984 gm.	19.67 %.
0.5008 gm.	0.1098 gm.		0.0984 gm.	19.65 %.
0.5009 gm.	0.1095 gm.		0.0982 gm.	19.60 %.
taken Ore	used KMnO_4^1	=	found Bi.	per cent.
0.5000 gm.	29.6 c.c.		0.0987 gm.	19.74 %.
0.3011 gm.	17.8 c.c.		0.0594 gm.	19.71 %.
0.3003 gm.	17.6 c.c.		0.0589 gm.	19.61 %.

The second ore was similar to the first. The same scheme of analysis was employed.

Results:

Ore taken	Bi_2O_3	=	found Bi.	per cent.
1.0002 gm.	0.0843 gm.		0.0756 gm.	7.55 %.
0.7506 gm.	0.0620 gm.		0.0556 gm.	7.41 %.
taken Ore	used KMnO_4^1		found Bi.	per cent.
0.7505 gm.	17. c.c.		0.0567 gm.	7.55 %.
0.5008 gm.	11.4 c.c.		0.0380 gm.	7.57 %.

¹ Factor 1 c.c. $\text{KMnO}_4 = 0.003335$ gm. Bi.

ANALYSIS OF COPPER MATTE CONTAINING
BISMUTH.

At the time these analyses were under way, no matte containing bismuth was on hand, so a convenient amount of Bismuthinite was mixed and ground up with a matte to make it about 0.5% to 0.6% bismuth. This was then analysed by the two methods as with ores.

The samples of matte were decomposed the same way for both methods, by nitric and hydrochloric acids and boiling. After dilution, the solution was saturated with hydrogen sul-

phide and the copper sulphide and bismuth sulphide contaminated with iron were filtered out and washed, and then dissolved in hot dilute nitric acid. From here the methods changed.

BASIC CARBONATE: The solution of the sulphides was treated with ammonia and ammonium carbonate to precipitate the bismuth and iron. These were then dissolved in acid and the bismuth was precipitated with hydrogen sulphide. This alternate treatment with ammonia and ammonium carbonate, and hydrogen sulphide had to be repeated several times to free the bismuth from copper and iron. The pure bismuth carbonate was then dissolved into a weighed porcelain crucible and ignited to Bi_2O_3 which was weighed.

MOLYBDATE METHOD: About 10 c.c. to 15 c.c. saturated solution of tartaric acid was added to the solution of the sulphides and this was then made alkaline with caustic potash. The bismuth hydroxide formed was dissolved by adding a slight excess of potassium cyanide. The solution was then saturated with hydrogen sulphide and the pure bismuth sulphide was filtered out and washed. One precipitation in this way was enough to get all the bismuth free from copper. This bismuth sulphide was dissolved in dilute nitric acid and precipitated as molybdate, which was treated as usual. For one determination in this way the standard KMnO_4 was diluted to one-tenth the strength to reduce the error in titration, as the amount of bismuth was so small.

Results :

taken Matte	found Bi_2O_3	used KMnO_4	per cent.
2.2433 gm.	0.0134 gm.		0.597%
2.5295 gm.	0.0164 gm.		0.648%
2.0004 gm.	0.0126 gm.		0.565%
2.2294 gm.		3.9 c.c.	0.583%
2.0032 gm.		3.25 c.c.	0.541%
2.0935 gm.		3.4 c.c.	0.542%
2.0020 gm.		34.2 c.c. $\frac{\text{standard}}{10}$	0.553%

The molybdate method was applied to the matte in the most unsatisfactory way, as only small samples were used. When,

however, enough sample is on hand in case of a matte low in bismuth, it is advisable to take 5 gm. to 10 gm. or more to start with, as no difficulty will be experienced separating the copper, and the bismuth will be enough for convenient handling by the molybdate method. Small amounts of bismuth are more difficult to precipitate as molybdate, and the titration is not as reliable when only a few c.c. of KMnO_4 are employed.

CONCLUSIONS.

The method proposed by Warwick and Kyle is founded on an old principle and the changes made by them make it worthless.

Bismuth is completely precipitated by hydrogen sulphide from a solution treated as follows: tartaric acid is added to the acid solution; it is then made alkaline with caustic potash and a slight excess of potassium cyanide is added. Under these conditions copper will remain in solution. Small amounts of bismuth are quickly and easily separated from large amounts of copper in this way.

Bismuth is completely precipitated as the molybdate $\text{BiNH}_4(\text{MoO}_4)_2$ by ammonium molybdate in a solution just acid with nitric acid. This precipitate can be washed with a 3% ammonium sulphate solution, and used for the determination of bismuth by dissolving in sulphuric acid, reducing the molybdenum and reoxidizing with KMnO_4 as in the method for phosphorus.

This separation and determination give a method equal in accuracy to the basic carbonate method, while the time necessary, especially when large amounts of copper are present is very much less.

BIOGRAPHICAL.

Herman S. Riederer entered the College of the City of New York in June, 1893, where he received the degree of B.S. in June, 1898. He entered Columbia University October, 1898, under the Faculty of Pure Science, studying for the degree of Ph.D. until October, 1902. He received the degree of A.M. in 1901, from Columbia University.

